



PCT/EP2004/005758



INVESTOR IN PEOPLE

REC'D	09 JUN 2004
WIPO	PCT

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Dated 20 May 2004

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)



1/77/2
05 JUN 03 5012675-1 C58642
PAI/7700 0.00 0312916.0

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

THE PATENT OFFICE

K

- 5 JUN 2003

The Patent Office

 Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference

NEWPORT

PAI 51097/GB

F 5 JUN 2003

2. Patent application number

0312916.0

3. Full name, address and postcode of the or of each applicant (*underline all surnames*)
 Imperial Chemical Industries PLC
20 Manchester Square
London W1U 3AN
Patents ADP number (*if you know it*)

6366090001

If the applicant is a corporate body, give the country/state of its incorporation

 935006
United Kingdom

4. Title of the invention

A MODIFIED BINDER POLYMER FOR COATING COMPOSITIONS

5. Name of your agent (*if you have one*)

Alan Victor COOPER

"Address for service" in the United Kingdom to which all correspondence should be sent (*including the postcode*)

 ICI Paints
Legal Department
Patent and Trade Marks Section
ICI Group Intellectual Property
P O Box 1883, Wexham Road
Slough PDO
Berkshire SL2 5FD
Patents ADP number (*if you know it*)

1014921002 7921901001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (*if you know it*) the or each application number

Country

Priority application number
(*if you know it*)Date of filing
(*day / month / year*)

N/a

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(*day / month / year*)

N/A

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (*Answer 'Yes' if*

Yes

- a) *any applicant named in part 3 is not an inventor, or*
- b) *there is an inventor who is not named as an applicant, or*
- c) *any named applicant is a corporate body.*

See note (d)

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.
Do not count copies of the same document

Continuation sheets of this form

Description

31

Claim(s)

Abstract

1 ✓ ✓

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

N

Translations of priority documents

N

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

1

Request for preliminary examination and search (Patents Form 9/77)

N

Request for substantive examination (Patents Form 10/77)

N

Any other documents
(please specify)

N

11.

I/We request the grant of a patent on the basis of this application.

Signature *Alan Victor Cooper*, Date *4 June 2003*
Alan Victor COOPER (Agent for Applicant)

12. Name and daytime telephone number of person to contact in the United Kingdom

A V Cooper 01753 877191

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

A MODIFIED BINDER POLYMER FOR COATING COMPOSITIONS

This invention relates to a modified film-forming binder polymer for a coating composition and to coating compositions containing the modified polymer. The modified polymer is especially useful in architectural coating compositions such as paints, varnishes or woodstains which can be applied

- 5 by brush, roller or pad at ambient temperatures of say 0 to 30°C to surfaces associated with buildings, furniture or fittings found in or around buildings.

For brevity, all such architectural coating compositions will be referred to as "paints".

All aqueous architectural paints contain film-forming binder polymer.

- 10 As a coating of liquid paint dries on a surface, this film-forming binder polymer serves to form a film (i.e. a dried coat) of paint which bonds to the surface and also binds together all the non-volatile components of the paint including particularly any opacifiers, pigments and extenders present.

A wide variety of conventional film-forming binder polymers are available, but those most commonly used in aqueous architectural paints are of three broad types obtained from mono-ethylenically unsaturated monomers and known colloquially as the "acrylics", the "vinyls" and the
5 "styrenics". The "acrylics" are usually copolymers of at least two alkyl esters of one or more mono-ethylenically unsaturated carboxylic acids (e.g. methyl methacrylate-butyl acrylate copolymer) whilst the "vinyls" usually comprise copolymers of a mono-vinyl ester of a saturated carboxylic acid and at least one of either an acrylic monomer or a different mono-vinyl
10 ester. The "styrenics" are copolymers containing styrene (or a similar mono-vinyl aromatic monomer) together with a copolymerisable monomer which is usually an acrylic.

Paints containing aqueous dispersions of particles of conventional film-forming binder polymers apply well to surfaces at warmer temperatures
15 of say above 10°C but if they are applied at low temperatures, the dried coats of paint formed are prone to cracking and consequently poor scrub resistance. Cracking occurs because the low temperatures impede the coalescence of the binder polymer particles into a film. Coalescence can be improved by adding organic so-called "coalescing solvents" to the paint
20 formulation and typical of such organic solvents are ethylene glycol, propylene glycol, benzyl alcohol and the proprietary solvent called

"Texanol" which is trimethylpentane diol isobutyrate. Nowadays such solvents are considered to be environmentally unfriendly and so an alternative solution to the cracking problem has been to use binder polymers having much lower glass transition temperatures (Tg) despite the known
5 disadvantages of such low Tgs. The first disadvantage is a reduction in scrub-resistance. The second disadvantage is that the tackiness associated with newly applied dried coats of paint persists for longer. Glass transition temperature, Tg, is defined in European Patent Specification EP 0 425 085A, the contents of which are herein incorporated by reference.

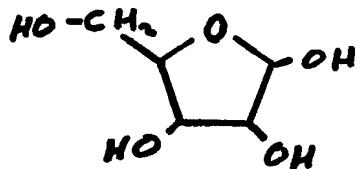
10 Opaque paints often contain particulate rutile titanium dioxide as an opacifier and/or as a white pigment. The rutile particles are coated with other oxides to minimise tendency for rutile to promote light induced degradation and so the rutile is expensive. Rutile also detracts from the scrub-resistance of a dried coat of paint if used in a high concentration in
15 the paint formulation.

It is an object of this invention to provide a modified film-forming binder polymer for a coating composition which at least minimises and usually avoids the need for the coating composition to contain an organic coalescing solvent without inducing film cracking or creating poor scrub-
20 resistance and persistent tackiness in a dried coat of paint. An alternative object is to promote the opacifying and pigmenting efficiency of rutile

especially so that less of it needs to be used in a formulation. Another object of the invention is to provide coating compositions containing the modified film-forming binder polymer.

Accordingly, this invention provides a film-forming binder polymer 5 for a coating composition wherein the polymer is modified by the presence of bonded moieties (preferably furanose moieties) obtainable from corn fibre gum. Corn is also known as maize. Furanose has the structural formula shown below where the asterisk denotes a very labile hydrogen which readily takes part in chemical reactions including bonding to

10



furanose

15 conventional monomers during polymerisation processes in which they form binder polymers. The lability of the asterisked hydrogen is described in an article by Gilbert et al. on Pages 1565 to 1572 of the Perkin Transactions (Volume 2) of the Journal of the Chemical Society of 1998, the contents of which Pages are herein incorporated by reference. It has 20 been found that coating compositions containing the modified binder polymer require minimal and usually zero amounts of an organic coalescing

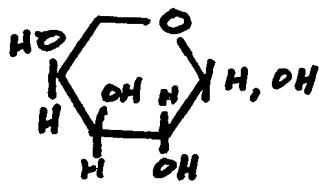
solvent yet do not suffer from significant film cracking, poor scrub resistance or excessively persistent tackiness in a dried coat of the composition. Also, the opacifying efficiency of rutile is improved.

Corn fibre gum is a well known product described for example in the
5 paper "Potential New Uses for Corn Fiber" given by K B Hicks et al during
the Proceedings of the Corn Utilization & Technology Conference, Kansas
City, USA held on 2 to 5 June 2002 and published by the National Corn
Growers Association and Corn Refiners Association, see pages 122 to 127.
The content of these pages is herein incorporated by reference. Hicks et al
10 report that corn fibre is a substantial by-product of corn milling from which
corn fibre gum can be extracted and has been extracted for at least 50 years.
A typical extraction comprises heating the corn fibre to 70°C in alkaline
hydrogen peroxide to yield the gum which can be spray dried to give a free
flowing powder which is easily re-dissolved in water. Details of a useful
15 extraction technique are given in United States Patent Specification
US 6 147 206 published on 14 November 2000, the contents of which are
herein incorporated by reference.

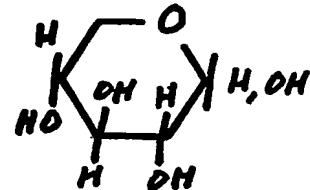
A typical corn fibre gum contains about 40wt% of arabinose (which
is an approximate equimolar mixture of furanose and pyranose) together
20 with about 50wt% of xylose and about 10wt% of a mixture of galactose,
gluconic acid, glucose, mannose, ribose and rhamnose. Galactose and

gluconic acid are present in a weight ratio of about 2:1. Pyranose and xylose have the structural formulae

5



pyranose



xylose

10

The simplest way to produce a modified binder polymer is to add corn fibre gum to the polymerisation reaction mixture from which the binder polymer is formed. Such polymerisations are conventionally performed with the aid of free radical or redox initiators at around 70 to 90°C. It is suspected that during the polymerisation, the initiators abstract

15

labile hydrogen from the furanose leading to a strong chemical bond between them and monomers taking part in the polymerisation. Preferably from 0.1 to 5wt% (and more preferably 2 to 4wt%) of corn fibre gum is added to the polymerisation reaction mixture where the percentages are based on the total weight of the monomers from which the binder polymer

20

is to be formed.

As indicated earlier, examples of suitable mono-ethylenically unsaturated monomers include:

- a) "acrylics" such as alkyl (especially methyl, ethyl, ethylhexyl and n-butyl) esters of unsaturated carboxylic acids such as acrylic or methacrylic or fumaric acids or maleic anhydride,
- b) "vinyls" such as mono-vinyl esters (especially vinyl acetate or vinyl "Versatate"¹) and
- c) "styrenics" which are usually styrene but which can be other monovinylidene aromatics such as vinyl toluene or vinyl pyridine and which are usually copolymerised with comonomers such as the ethyl or ethylhexyl or butyl acrylics mentioned above.

10 Various mono-ethylenically unsaturated acid or acid anhydride monomers may be copolymerised with the binder monomers to increase the hydrophilic character of the binder polymer in alkaline solutions and so increase the stability of the dispersions. However the acid comonomers usually do not exceed 7 mol % of the total monomers for otherwise the

15 binder polymer becomes too hydrophilic to retain acceptable scrub-resistance. Suitable acids include unsaturated carboxylic acids and in particular acrylic or methacrylic acids and unsaturated acid anhydrides include maleic anhydride. Acids or their anhydrides may allow some bonding of the binder polymer by ester formation to other hydroxylic

¹ Vinyl "Versatate" is the vinyl ester of so-called "Versatic" acid which is a mixture of aliphatic monocarboxylic acids each containing an average of 9, 10 or 11 carbon atoms and is commercially available from the Shell Chemical Company of Carrington, England.

moieties in the corn fibre gum in addition to the bonding to furanose by means of labile hydrogen.

If copolymerisation at superatmospheric pressures is commercially tolerable, the hydrophilic nature of the binder polymer can be adjusted
5 downwards by including some mono-olefin (usually some ethylene) in the monomers. This will improve scrub-resistance.

It is desirable to choose combinations of monomers which include a sterically bulky monomer so as to result in binder polymers in which the chain moieties have a Tg of below 350K and preferably below 325K.

10 Preferred "acrylic" binder copolymers include copolymers of methyl methacrylate with butyl or 2-ethylhexyl acrylate as sterically bulky monomers and optionally copolymerised with up to 7 mol % acrylic or methacrylic acid. Preferred "vinyl" binder copolymers include copolymers of vinyl acetate with a bulky monomer which is usually vinyl "Versatac" or
15 bulky acrylic monomer as above plus the same optional acid comonomers.

Preferred "styrenic" binder copolymers include copolymers of styrene with butyl or 2-ethylhexyl acrylate serving as the bulky monomers with optionally up to 7 mol % acid comonomers as above. Tg will be increased unacceptably by excessive crosslinking and so it is essential not to
20 incorporate more than 7 wt % of a conjugated diene into the binder polymer and it is very much preferred to avoid any such diene.

The efficiency of the rutile opacification achieved using acrylic binder polymers can be further improved by prepolymerising small amounts of vinyl monomers before a main polymerisation of acrylic or vinyl monomers.

5 An aqueous dispersion of the modified film-forming binder copolymer is easily converted into a coating composition by mixing it with all the components of the composition except for any chelate structuring agent. If a strongly structured composition, the chelate should be stirred in just before the composition is filled into cans so that the gel structure 10 develops in the can. The most significant of the other components are opacifiers (usually rutile or sometimes anatase titanium dioxide or voided organic polymer particles), other pigments and also extenders which are solid particles which serve to space apart the opacifiers and pigments. Typical extenders are chalk, limestone, kaolin and talc. Silica may also be 15 present as a matting agent. Whilst this invention is of most importance in making paints, it is also possible to omit the opacifier to produce a varnish or woodstain. The coating compositions preferably have a "Rotothinner" (low shear) viscosity of from 0.15 to 2.0 pascal.sec all measured at 25°C. A strongly structured thixotropic composition preferably has a gel strength at 20 1 week of at least 50g.cm.

The use of the modified binder polymer in a coating composition improves the efficiency of particulate inorganic ingredients in the formulation. In particular, it has been found possible to increase the opacifying efficiency of rutile by from 10 to 15% so allowing a greater 5 opacity to be achieved or alternatively allowing reduced concentrations of rutile with a consequent improvement in scrub-resistance and cost.

The invention will now be illustrated by the following Examples of which Examples A to C are comparative.

The paints were tested for opacity and scrub-resistance as follows:

10 ISO Opacity Test:

A clean transparent polypropylene sheet 280 mm long by 104 mm wide is mounted on a clean transparent glass plate using adhesive tape. The sheet provides a surface to which a coat of paint under test can be applied.

15 The paint under test is passed through an 80 μm nylon mesh filter to remove any poorly dispersed particles and then it is de-aerated under vacuum. Any surface skin should be removed.

A coat of the de-aerated paint is applied to the polypropylene surface using a 175 μm block spreader (1 μm equals 10^{-6} m) and the coat is allowed to dry at room temperature for 16 hours. Next, the dried coat is 20 inspected for defects by placing the glass plate over a light box and any defective coats must be rejected.

The CIE X, Y, Z values of the dried coat are determined using a spectrophotometer calibrated against a standard white and a standard black tile. The X, Y, Z values are then used to calculate the Kubelka-Munk Scatter Coefficient which is a good indication of opacity.

5

ISO Scrub Resistance Test:

A coat of paint is applied to each of four polypropylene panels as in the opacity test above except that a 400 µm block spreader is used. The coats are allowed to dry for 28 days at 23°C in a 50% humidity. Next the

10 dried coated panels are weighed, subjected to 200 cycles of rubbing in accordance with the ISO Scrub Test, EN 13300 Part 5.4, ISO 11998 and weighed again. The average weight loss for the four panels was taken and, together with the area of the rubbed surface and the density of the coat, was used to calculate the loss of thickness of the coat. This calculated loss of
15 thickness is an inverse indication of scrub-resistance.

The ISO Test gives scrub-resistances numerical ratings as follows:

	<u>Loss of Thickness</u>	<u>No. of Cycles</u>	<u>Rating</u>
20	Below 5µm	200	1
	5 to 20µm	200	2
	20 to 70µm	200	3
	Below 70µm	40	4
	Above 70µm	40	5

British Scrub Resistance Test:

5 The British Scrub Resistance Test is performed according to British Standard 7719 of 1994 and a weight loss is reported instead of a calculated loss of thickness.

“Bentone” Ew: Bentonite clay supplied by Rheox Ltd of UK

“Dispelair” CF 246: A surfactant supplied by Blackburn Chemicals Ltd of

10 Blackburn, UK

“Disponil” A1580: A surfactant supplied by Henkel Performance Chemicals of Germany

15 “Blanose” 7M 31C: A cellulosic thickener supplied by Hercules Inc of USA

“Britomya” V: A calcium carbonate supplied by OMYA UK Ltd of Surrey, UK

20 “Dispex” N40: A surfactant supplied by Allied Colloids of UK

“Empimin” OT75: A surfactant supplied by Albright & Wilson of UK

“Fordacal” 30: A calcium carbonate extender supplied by Foramin Co. Ltd of UK.

25 “Lubrizol” 2405: A surfactant supplied by Lubrizol UK LTD of UK

“Mergal” 711 K6: A biocide supplied by Troy Chemicals Europe BV of the Netherlands.

"Microdol" H 200: Dolomite supplied by Omya of Cologne, Germany.

"Natrosol" 250MR: A cellulosic thickener supplied by Hercules Inc of USA

5

"Perlankrol" ESD60: A surfactant supplied by Akzo Nobel Chemicals Ltd of the Netherlands

"Rhodacal" A246L: A surfactant supplied by Rhodia SA of France

10 "Ropaque" ULTRA: A voided organic particulate opacifier supplied by Rohm & Haas of USA

"Tilcom" AT35: A chelate structuring agent supplied by Tioxide Specialists Ltd (Huntsman) of Teeside, UK

15

EXAMPLE 1

Production of a Modified Acrylic Binder Polymer:

Four preliminary charges were made up which will be referred to as

5 the corn fibre gum charge, the seed monomer charge, the initiator charge (which was subsequently divided into three sub-charges) and the acrylic monomer charge. The corn fibre gum charge was made up by mixing together the following components:

	<u>Component</u>	<u>Weight g</u>
10	Water	549.77
	Corn Fibre gum	12.60
	Sodium bicarbonate	1.20
	Sodium chloride (pure and vacuum dried)	1.02
	Surfactant Rhodacal A246L	<u>1.44</u>
15	Total Corn Fibre gum charge	566.03

The seed monomer charge was made up by mixing together the following components:

	<u>Component</u>	<u>Weight g</u>
20	Vinyl Acetate	20.77
	Vinyl "Versatake"	3.67
	Surfactant "Empimin" OT75	<u>0.25</u>
	Total Seed Monomer Charge	24.69

The initiator charge was made up by mixing together the following components:

	<u>Component</u>	<u>Weight g</u>
	Water	34.00
5	Ammonium persulphate	<u>1.60</u>
	Total initiator charge	35.60

The initiator charge was then divided into three sub-charges. 45wt% of the charge became the seed initiator charge to which was then added 0.49g of the surfactant "Lubrizol" 2405. Another 45wt% of the charge became the 10 main initiator charge and the remaining 10wt% became the "mop-up" initiator charge.

The acrylic monomer charge was made up by mixing together the following components one after another in the order shown in the list below:

15	<u>Component</u>	<u>Weight g</u>
	Methyl methacrylate	229.10
	Surfactant "Disponil" A1580	18.85
	Surfactant "Perlankrol" ESD60	2.86
20	2-ethylhexyl acrylate	<u>219.62</u>
	Total Acrylic Monomer Charge	470.43

In performing the polymerisation, the corn fibre gum charge was first purged with nitrogen for 5 minutes and then heated to 75°C and then held at that temperature for 30 minutes. The seed monomer charge was then added to the hot corn fibre gum charge and the whole was maintained at 75°C for a

further 10 minutes. The seed initiator sub-charge was then added and the temperature of the combined charges was increased to 90°C over 30 minutes during which time an aqueous dispersion of vinyl acetate/vinyl "Versatake" seed copolymer formed with possibly some bonding of moieties from the
5 corn fibre gum.

The acrylic monomer charge together with the main initiator sub-charge were added dropwise over a period of two hours to the dispersion of seed copolymer whilst the temperature was maintained at 90°C. During this time, an aqueous dispersion of seeded copolymer of methyl methacrylate
10 and 2-ethylhexyl acrylate formed with bonding of moieties from the corn fibre gum. On completion of the addition of the acrylic monomers, the "mop-up" initiator sub-charge was added and the temperature maintained at 90°C for a final 30 minutes after which the dispersion was allowed to cool to 37°C. The dispersion consisted of particles of seeded acrylic copolymer
15 containing 2.5wt% of bonded corn fibre moieties which had bonded either during the seed copolymerisation or during the main polymerisation and quite probably during both. In the copolymer, 5wt% was vinyl seed and the ratio of copolymerised methyl methacrylate to 2-ethylhexyl acrylate was 1:1.

20 A solution of 1.5g an isothiazoline based biocide in 4g water was added to the cooled dispersion.

EXAMPLE 2

Production of a Modified Vinyl Binder Polymer:

Five preliminary charges were made up which will be referred to as the corn fibre gum charge, the initiator charge (which was subsequently divided into three sub-charges), the vinyl monomer charge, the oxidant charge and the reductant charge. The corn fibre gum charge was made up by mixing together the following components:

	<u>Component</u>	<u>Weight g</u>
10	Water	423.96
	Corn Fibre gum	12.62
	Sodium bicarbonate	1.20
	Surfactant Rhodacal A246L	<u>1.44</u>
	Total Corn Fibre gum charge	439.22

15 The initiator charge was made up by mixing together the following components:

	<u>Component</u>	<u>Weight g</u>
20	Water	39.66
	Ammonium persulphate	1.70
	Surfactant "Lubrizol" 2405	<u>2.17</u>
	Total initiator charge	43.53

The initiator charge was then divided into three sub-charges. 30wt% of the charge became a seed initiator charge. Another 50wt% of the charge became the main initiator charge and the remaining 20wt% became a "mop-up" initiator charge.

The vinyl monomer charge was made up by mixing together the following components one after another in the order shown in the list below:

	<u>Component</u>	<u>Weight g</u>
5	Vinyl Acetate	415.96
	Surfactant "Empimin" OT75	5.06
	Vinyl "Versatate"	<u>73.40</u>
	Total Vinyl Monomer Charge	494.42

The oxidant charge was made up by mixing together the following 10 components:

	<u>Component</u>	<u>Weight g</u>
	Water	4.71
	Tertiary butyl hydroperoxide	<u>1.00</u>
	Total Oxidant Charge	5.71

15 The reductant charge was made up by mixing together the following components:

	<u>Component</u>	<u>Weight g</u>
20	Water	6.81
	Sodium metabisulphite	<u>1.00</u>
	Total Reductant Charge	6.81

In performing the polymerisation, the corn fibre gum charge was first purged with nitrogen for 5 minutes and then heated to 65°C and maintained 25 at that temperature for 30 minutes. 2.5wt % of the vinyl monomer

charge was then added to the hot corn fibre gum charge as a seed quantity and the whole was maintained at 65°C for 10 minutes. The seed initiator sub-charge was then added and the temperature of the combined charges was raised to 85°C for 30 minutes during which time an aqueous dispersion 5 of vinyl acetate/vinyl "Versatac" seed copolymer formed with possibly some bonding of moieties from the corn fibre gum.

The remaining vinyl monomer charge together with the main initiator sub-charge were added dropwise over a period of three hours to the dispersion of seed copolymer whilst the temperature was maintained at 10 85°C. During this time, an aqueous dispersion of seeded copolymer of vinyl acetate and vinyl "Versatac" formed with bonding of moieties from the corn fibre gum. On completion of the addition of the vinyl monomers, the "mop-up" initiator sub-charge was added and the temperature maintained at 85°C for a final 30 minutes. Next the oxidant charge was added and the 15 temperature maintained at 70°C for 5 minutes and then the temperature was reduced to 60°C and the reductant charge was added and the temperature was maintained at 60°C for a further 5 minutes. The dispersion was allowed to cool to 37°C and was found to consist of particles of seeded vinyl copolymer to which corn fibre moieties had bonded either during the seed 20 copolymerisation or during the main polymerisation and quite probably during both.

A solution of 1.7g an isothiazolaoline based biocide in 6.61g water was added to the cooled dispersion.

EXAMPLE 3
AND
5 COMPARATIVE EXAMPLE A

Preparation and Testing of Acrylic Silk Paint:

An acrylic silk paint (i.e. paint having a low pigment volume concentration or "PVC" of 20.5%) was prepared using either the aqueous dispersion of modified acrylic binder copolymer made in Example 1 (Example 3) or an aqueous dispersion made according to Example 1 except that the corn fibre gum was omitted from the copolymerisation (Comparative Example A) together with the ingredients as listed in Table 1. The paint was then tested for opacity and ISO scrub-resistance and the 15 results are given in Table 2.

In Example 3, a millbase of water, extenders, rutile and various other additives was made using a "Dispermat" rotatable blade mixer in which the blade was rotated at 300 rpm for low speed mixing and at 3 000 rpm for high speed mixing. To begin, the ingredients for Example 3 in 20 Batch A in Table 1

TABLE 1
INGREDIENTS FOR ACRYLIC SILK PAINTS

Example		3	A
Ingredient and Amount Used		g	g
BATCH A			
Water		135	172
“Bentone” EW		2.9	2.9
bentonite clay			
“Displex” N4D		1.9	1.9
surfactant			
“Dispelair” CF 246		1.0	1.0
antifoaming agent			
“Mergal” 711K6		1.5	1.5
biocide			
BATCH B			
“Britomya” V		54.5	54.5
calcium carbonate			
Rutile TR92		144	164
BATCH C			
Water		31	31
“Blanose” 7M31C		4.5	6.4
cellulosic thickener			
Water		73.3	73.3
“Dispelair” CF246		1.0	1.0
antifoaming agent			
Water		10.0	10.0
BATCH D			
*Aqueous dispersion of binder copolymer		503	450
Ammonia		0.2	0.2
“Dispelair” CF246		1.0	1.0
antifoaming agent			
“Tilcom” AT35		2.0	2.0
structuring agent			
Water		--	30

* The concentrations of the copolymer in the dispersion were adjusted to ensure that both paints had a PVC of 20.5%.

were added to the mixer at subjected to low speed mixing for 10 minutes.

5 Next, the ingredients of Batch B were added to the contents of the mixer and all were subjected to high speed mixing for 20 minutes. Next, the first quantity of water and the "Blanose" of Batch C were added to the contents of the mixer and all were subjected to high speed mixing for 10 minutes. Then the second quantity of water and the "Dispelair" of Batch C were
10 added to the contents of the mixer and all were subjected to high speed mixing for 10 minutes. Finally the millbase was completed by adding the last quantity of watch from Batch C and subjecting the contents of the mixer to low speed mixing.

The silk paint was made by adding the ingredients of Batch D in turn
15 to the millbase in the mixer whilst maintaining low speed mixing. First the aqueous dispersion of acrylic binder copolymer was added slowly over a period of five minutes. Then the other ingredients were added one after another to complete the paint. The paint was allowed to stand for 16 hours at room temperature to enable the "Tilcom" to create structure and then the
20 paint was ready for subjecting to the opacity and ISO scrub resistance tests the results obtained are shown in Table 2.

TABLE 2
OPACITY AND SCRUB-RESISTANCE
TEST RESULTS (ACRYLIC SILK PAINTS)

5

Example	Rutile Content g	'Blanose' Content g	Kubelka- Munk Scatter Coefficient	ISO Scrub Resistance	
				Thickness Lost μm	ISO Rating
3	144	4.5	8986	1.0	1
A	164	6.4	9061	2.9	1

10

EXAMPLE 4
AND
COMPARATIVE EXAMPLE B

Preparation and Testing of Acrylic Matt Paint:

An acrylic matt paint (i.e. paint of high PVC of 62.8%) was prepared
 15 using a procedure similar to that employed for Example 3 but using
 ingredients as specified in Table 3. As in Example 3 relating to silk paint,
 Example 4 employed the aqueous dispersion of acrylic binder copolymer
 made in Example 1 whilst Comparative Example B employed the
 corresponding unmodified acrylic copolymer.

20

TABLE 3

INGREDIENTS FOR ACRYLIC MATT PAINTS

Example	4	B
Ingredient and Amount Used	g	g
BATCH A		
Water	150	150
"Displex" N40 surfactant	3.1	3.1
"Dispelair" CF246 antifoam agent	1.0	1.0
"Meral" 711 K6 biocide	1.5	1.5
BATCH B		
"Britomya" V calcium carbonate	55	55
"Fordacal" 30	123	123
China clay supreme	57	57
Rutile TR92	126	143
BATCH C		
Water	130	130
"Natrosol" cellulosic thickener	5.0	6.7
Water	42.8	42.8
"Dispelair" CF 246	1.0	1.0
BATCH D		
Aqueous dispersion of binder copolymer	207	173
"Ropaque" voided particle opacifier	8.1	8.1
"Dispelair" CF 246	1.0	1.0
"Tilcom" AT35 structuring agent	4.0	4.0
Water	--	26

In Example 4, a millbase was made by adding the ingredients of

5 Batch A, Table 3 to a "Dispermat" mixer. The contents of the mixer were subjected to 10 minutes of low speed (300 rpm) mixing and then the ingredients from Batch B were added slowly and the whole subjected to high speed (3 000 rpm) mixing for 20 minutes. Next the first quantity of water and the "Natrosol" from Batch C were slowly added to the contents of

the mixer and the whole were subjected to 10 minutes of high speed mixing. Finally the millbase was completed by adding the last quantity of water and the "Dispelair" from Batch whilst subjecting all the contents to slow speed mixing.

5 The matt paint was made by adding the ingredients of Batch D in turn to the millbase in the mixer whilst maintaining the slow speed mixing. First the aqueous dispersion of the acrylic binder copolymer was added slowly over a period of five minutes. Then the other ingredients from Batch D were added one after another to complete the paint. The paint was allowed
10 to stand for 16 hours at room temperature to enable the "Tilcom" to create some structure and then paint was ready for subjecting to the opacity and ISO scrub-resistance tests.

In Comparative Example B the procedure was repeated but using the corresponding unmodified acrylic copolymer. The paints were subjected to
15 the opacity and ISO scrub-resistance tests and the results are shown in Table 4.

TABLE 4

**OPACITY AND SCRUB-RESISTANCE
TEST RESULTS (ACRYLIC MATT PAINTS)**

Example	Rutile Content g	“Natrosol” Content g	Kubelka- Monk Scatter Coefficient	Scrub Resistance	
				Thickness Lost μm	ISO Rating
4	126	5.0	10633	15.2	2
B	143	6.7	10431	17.8	2

5

**EXAMPLE 5
AND
COMPARATIVE EXAMPLE C**

10

Preparation and Testing of Vinyl Matt Paint:

A vinyl matt paint (i.e. paints of high PVC of 45%) was prepared using a procedure similar to that employed for Example 4 but using the dispersion of modified vinyl binder copolymer made in Example 2 and the ingredients as specified in Table 5 whilst Comparative Example C employed the corresponding unmodified vinyl binder polymer.

15

20

TABLE 5

INGREDIENTS FOR VINYL MATT PAINTS

Example	5	C
Ingredient and Amount Used	g	g
BATCH A		
Water	150	150
“Bentone” EW bentonite clay	2.0	2.0
“Displex” N40 surfactant	2.0	2.0
“Dispelair” CF246 antifoam agent	0.5	0.5
“Meral” 711 K6 biocide	0.5	0.5
“Disponil” A1580:A surfactant	5.0	5.0
BATCH B		
“Micropdol” H 200 dolomite	39	39
“Fordacal” 30	74	74
China clay	49	49
Rutile TR92	133	133
BATCH C		
Water	150	150
“Blanose” cellulosic thickener	5.0	6.5
Water	120	120
BATCH D		
“Dispelair” CF 246	0.5	0.5
Biocide	0.2	0.2
Water	10	10
Aqueous dispersion of vinyl binder copolymer	300	300
Ammonia to pH 8.5	0.04	0.04
“Ropaque” voided particle opacifier	48	48
“Dispelair” CF 246	1.6	1.6

5

In Example 5, a millbase was made by adding the ingredients of Batch A, Table 3 in turn to a “Dispermat” mixer. The contents of the mixer were subjected to 10 minutes of low speed (300 rpm) mixing and then the

ingredients from Batch B were added slowly in turn and the whole subjected to high speed (3 000 rpm) mixing for 20 minutes. Next the first quantity of water and the "Blanose" from Batch C were slowly added to the contents of the mixer and the whole were subjected to 10 minutes of high
5 speed mixing. Finally the millbase was completed by adding the last quantity of water from Batch C whilst subjecting all the contents to slow speed mixing.

The matt vinyl paint was made by adding the first amount of "Dispelair", biocide and water of Batch D in turn to the millbase in the
10 mixer whilst maintaining the slow speed mixing. Next the aqueous dispersion of the vinyl binder copolymer was added slowly with the ammonia (to achieve a pH of 8.5) over a period of five minutes. Then the "Ropaque" and second amount of "Dispelair" from Batch D were added one after another with slow mixing to complete the paint. The paint was
15 subjected to the British scrub-resistance test and coats of the paints 400µm thick which had dried at below 8°C were examined visually for cracking.

In Comparative Example C the procedure was repeated but using the corresponding unmodified vinyl binder copolymer. The results the British scrub-resistance test and the visual examination are shown in Table 6.

TABLE 6

Example	Weight lost in British Scrub Test mg/cm ²	Observation of Cracking
5	1.64	Major Cracking
C	1.47	No Cracking

Tables 2, 4 and 6 show that the scrub-resistances of the paints
 5 containing modified and unmodified binder copolymers were, within
 experimental error, about equal. Tables 2 and 4 show that the opacifying
 efficiency of the rutile was improved by the use of the corn fibre gum
 modified binder polymer . Table 6 shows that the use of the corn fibre gum
 modified binder polymer overcomes the need to use coalescing solvents to
 10 prevent the cracking of coats of paint applied at low temperatures.

It was also observed that the tackiness of the dried coats of the paints
 according to Examples 3, 4 and 5 was lost at about the same rate as for
 commercial paints containing coalescing solvents.

CLAIMS

1. A film-forming binder polymer for a coating composition wherein the polymer is modified by the presence of bonded moieties obtainable from corn fibre gum.

5

2. A binder polymer as claimed in Claim 1 wherein the polymer is modified by bonded moieties derived from furanose.

3. A binder polymer as claimed in Claim 1 or Claim 2 wherein the
10 bonded moieties are derived by adding corn fibre gum to the polymerisation process by which the binder polymer is formed.

4. A binder polymer according to Claim 2 wherein the binder moieties derived from furanose are derived by having furanose present during the
15 polymerisation process which produces the binder polymer.

5. A process for modifying film-forming binder polymers which are binder polymers for coating compositions wherein corn fibre gum is added to the polymerisation reaction which produces the binder polymer.

6. A process for modifying film-forming binder polymers which are binder polymers for coating compositions wherein furanose is added to the polymerisation reaction which produces the binder polymer.
- 5 7. A coating composition wherein the composition contains a modified binder polymer as claimed in any one of the preceding claims
8. A coating composition according to Claim 7 wherein the composition contains rutile.

10

9. A method for improving the efficiency of particulate additives for coating compositions wherein the method comprises employing a modified binder polymer as a binder in a coating composition containing the particulate additives.
- 15 10. A method according to Claim 10 wherein the particulate additive is rutile.

ABSTRACT

5 A film-forming binder polymer for a coating composition such as a
paint, varnish or woodstain where the polymer is modified by the presence
of bonded moieties derived from corn fibre gum, especially moieties
derived from furanose. The modified binder polymer minimises the need to
use coalescing solvents without creating excessive tackiness and improves
10 the scrub resistance of dried coats of paint and also improves the efficiency
of particulate additives such as rutile.